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Biogenic silver nanocomposite polyethersulfone UF membranes with antifouling properties

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ABSTRACT

Biofouling remains one of the most challenging issues of membrane application in water industry. One of the practical strategies to control fouling is anti-biofouling membrane. High concentration and high stable biogenic nanoparticle silver with the averaged diameter of only 6 nm (Bio-Ag^0-6) was firstly extracted from the supernatant of *Lactobacillus fermentum*. The biogenic nanocomposite polyethersulfone (Bio-Ag^0-6/PES) membranes were prepared by adding different amounts of biogenic nanoparticle silver into the dope solution. The nanocomposite membranes were systematically tested for physical properties with pure water permeability, MWCO (molecular weight cut-off), contact angle, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results demonstrated that the Bio-Ag^0-6 nanoparticles well dispersed into PES matrix without aggregation. Bio-Ag^0-6 slightly increased the hydrophilicity of the PES membranes, improved the water permeability and did not sacrifice the selectivity of BSA. The protein adsorption on the membrane surface decreased significantly due to the increased hydrophilicity and the improved smoothness of membrane surfaces. The evaluation of silver release from the composite membranes indicated the good stability of immobilized Bio-Ag^0-6 in the membranes. The results of disk diffusion test revealed the excellent antibacterial activity of the nanocomposite membranes. In addition, the sludge immersion and the bacterial suspension filtration experiments showed that the Bio-Ag^0-6/PES composite membranes not only prevent the bacteria attachment on the membrane surface but also inhibit the reproduction and development of biofims. The Bio-Ag^0-6/PES composite membranes were considered to be an effective strategy to decrease the biofouling in the membrane process.

1. Introduction

The ultrafiltration (UF) process is an attractive technology due to low capital cost, small footprint, low operation pressure and no phase change during the filtration process [1,2]. Membrane fouling, especially biofouling, remains one of the most challenging issues in membrane separation processes which hinder wider applications of UF in wastewater treatment system [3,4]. Biofouling takes place through a series of steps including the attachment of microorganisms on the membrane surface, accumulation of assimilable organics, multiplication, colony formation and finally biofilm maturation [5]. As the most complicated fouling, biofouling usually causes various negative effects on membrane performances such as flux decline, increment of operation or maintenance costs and membrane degradation [6,7]. Therefore, many efforts have been made to develop anti-fouling strategies.

To reduce biofouling, functional membranes containing biocides or antibacterial materials have attracted tremendous interest. Silver is one of the most widely studied biocides because of its excellent biocidal properties [8,9]. Silver nanoparticles have been successfully introduced into various membrane materials such as polysulfone [2,10,11], polyethersulfone [12–15], polyvinylidene fluoride [16,17], polyamide [18,19] and chitosan [20–22]. The addition of silver nanoparticles into the polymer membranes improved the membrane performance in terms of their flux and fouling resistance, attributing to an increase of hydrophilicity or change in membrane morphology. However, the chemically produced silver nanoparticles often have problems with particle stability. The beneficial effects of added particles are often limited by aggregation and poor compatibility with the polymeric matrix [6,7]. Besides the improved durability of silver-containing membrane and the simultaneously reduced potential risks of released silver ions at high load to the environment and filtration process are still challenges for excellent membrane performance.

Recently, biosynthesis of silver nanoparticles as an environment-friendly method has attracted increasing attention. In our previous

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study, biogenic silver nanoparticles with the mean size of 11 nm (denoted as Bio-Ag^0-11) was introduced into PES membranes (Bio-Ag^0-11/PES). The attachment of the nanoparticles with the micro scale surface of the bacterium on which they were formed prevents them from aggregating [6,7]. However the large amount of existed biomass not only significantly decreased the pure silver content in the biogenic silver (150 mgAg g^{-1}) but also decreased the compatibility with PES matrix as shown that many silver-containing microstructures dispersed on the membrane surfaces. Besides the reduced compatibility of nanoparticles enhanced the silver leaching in the filtration test which may increase the potential risks to the environment.

Herein, we improved a novel biogenic silver nanoparticles with an average size of only 6 nm (Bio-Ag^0-6), extracted from the supernatant of *Lactobacillus fermentum* and no attachment to any whole bacteria cells. The fabrication method, the size and the morphology of nanoparticles were quite different from our previous report [23]. The modified synthesis largely improved the silver content from 150 mgAg g^{-1} to 450–500 mgAg g^{-1}. The main objective of this study is to fabricate and characterize properties of the Bio-Ag^0-6/PES mixed matrix membranes. The silver release from the nanocomposite membranes in both static immersion and dead-end filtration tests was assessed. Furthermore, we studied the effect of silver release on the filtration performance of the nanocomposite membranes. The antibacterial and antibiofouling performances were evaluated by the disk diffusion method, activated sludge immersion test as well as bacterial suspension filtration experiment.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES, E6020P, BASF Co., Germany) was dried at 120 °C overnight in a vacuum oven prior to dope preparation. N, N-Dimethylacetamide (DMAC) was obtained from Shanghai Jinshan Jingwei Chemical Co., Ltd. Silver standard solution (1000 mg L^{-1}) was supplied by Sinopharm Chemical Reagent Co., Ltd. The standard constituents of the Luria-Bertani medium and agar plates used for bacteria incubation were purchased from Oxoid Co., Ltd. Trypsin (24 KDa), pepsin (35 KDa), egg albumin (45 KDa) and Bovine serum albumin (BSA, 69 KDa) was obtained from Solarbio Science & Technology Co., Ltd. The ultrapure water used in all experiments was supplied by a Milli-Q system (Millipore Corp., USA).

2.2. Synthesis and characterizeation of biogenic silver (Bio-Ag^0-6)

Biogenic silver (Bio-Ag^0-6) was synthesized with *Lactobacillus fermentum LMG 8900*, provided by Laboratory of Microbial Ecology and Technology (LabMET), Ghent University in a modified method. The detailed preparation process and characterization of Bio-Ag^0-6 have been reported in the previous paper [24].

2.3. Preparation of composite membranes

Different amounts of dry Bio-Ag^0-6 were added to DMAC and ultrasonicated for 30 min for well dispersion. Then PES was dissolved in the solvent while stirring for 24 h at 60 °C until a homogeneous solution was obtained. The casting solution was degassed at 60 °C overnight without stirring to completely remove air bubbles. The solution was cast on a non-woven support with a casting knife gap setting of 200 μm. The fresh membrane was immediately immersed in the deionized water bath at room temperature to induce phase separation. After coagulation, the membranes were transferred to fresh distilled water to remove all the residual solvent before characterization. Table 1 shows the composition of all the membranes prepared in the study.

Table 1
The composition and the basic parameters of nanocomposite membranes.

Membrane no.	Silver content (wt%)	CA (°)	porosity (%)	MWCO (KDa)	Water uptake (%)
M0	0	68.9	74.9	45	59.5 ± 2.1
M1	0.1	60.8	76.3	45	62.6 ± 1.5
M2	0.3	57.5	76.8	45	62.9 ± 1.3
M3	0.5	54.7	77.3	45	65.2 ± 2.4
M4	1.0	54.6	75.7	45	65.3 ± 1.7

2.4. Membrane characterization

Morphological structures of the prepared membranes were examined using a scanning electron microscopy (FESEM) (HITACHI S-4800). For the cross-section observation, the membrane samples were frozen and fractured in liquid nitrogen. All the samples were sputtered by gold for observation. Presence of silver nanoparticles was confirmed by energy dispersive X-ray spectra (EDX) and elemental mapping (see Supporting information).

The surfaces of membranes were scanned in a scan size of 5 μm × 5 μm by atomic force microscopy (AFM) to determine the roughness of membranes. The surface roughness parameters which are expressed in terms of the mean roughness (Sa) and the root mean square roughness (Sq) were calculated from AFM images.

The hydrophilicity of all the membrane surfaces was characterized by contact angle goniometer (DSA100, German KRUSS). At least five contact angles at different locations were recorded to get a reliable value.

The membrane porosity $\varepsilon(\%)$ was defined as the ratio between the volume of the pores and the total volume of the membrane. For porous membranes, it could be determined by a gravimetric method, determining the weight of liquid contained in the membrane pores [27]:

$$\varepsilon(\%) = \frac{(W_w - W_d)/D_w}{(W_w - W_d)/D_w + W_d/D_p} \times 100\% \quad (1)$$

where ε is the porosity of membrane (%), W_w is the wet sample weight (g), W_d is the dry sample weight (g), D_w (0.998 g cm^{-3}) and D_p (0.37 g cm^{-3})are the density of the water and polymer, respectively.

Water uptake tests were conducted to evaluate the adsorption capability of water to membranes with biogenic silver (Bio-Ag^0-6). Pieces of different membrane samples were immersed in Milli-Q water at room temperature for 24 h and the weight of wetted membrane W_w was measured after dabbing it with a filter paper. The dry weight W_d was determined after 24 h drying at 60 °C. The water uptake ratio was calculated with Eq. (2):

$$U = \left(\frac{W_w - W_d}{W_w}\right) \times 100\% \quad (2)$$

2.5. Filtration performance of composite membranes

A dead-end filtration cell (Model 8010, Millipore Corp. USA) was used to evaluate the filtration performance of membranes. The effective area of the membrane was 4.1 cm^2. All the experiments were performed at room temperature (25 ± 1 °C). To measure the pure water permeation, the membranes were initially compacted at 0.2 MPa for 30 min, and then the cumulative permeate weight was measured by an electronic balance (Sartorius BS224S, Germany) with Wedge software. The permeate